Fractionation of Tallow Fatty Acids.

Preparation of Purified Oleic Acid and an Inedible Olive Oil Substitute

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THE starting material usually employed in the laboratory preparation of purified oleic acid (oleic acid content, over 95%) is olive oil (1) since it not only contains a high percentage of oleic acid, but, what is probably more important, it also has a high ratio of oleic to linoleic acid (about 10:1). For the industrial preparation of purified oleic acid, however, olive oil is too expensive, and only relatively small quantities are available for non-edible uses. In a recent publication from this laboratory (2) we described a procedure for the preparation of purified oleic acid from red oil (commercial oleic acid) by low-temperature, solvent crystallization. Although red oil is inexpensive and readily available and is rich in oleic acid, its ratio of oleic to linoleic acid is rather low (usually less than 5:1). When such a large proportion of linoleic acid is present, its solubilizing effect causes considerable loss of oleic acid during the low-temperature crystallization. A more satisfactory starting material is one which is not only inexpensive and readily available in large quantities but which also has a high ratio of oleic to linoleic acid (at least 8:1). An examination of the fatty acid composition of various common fats and oils reveals that tallow meets these requirements.

Superficially, it would appear that tallow would be unsatisfactory as a starting material for the preparation of purified oleic acid since it usually contains only 45 to 50% oleic acid and its content of saturated acids is rather high (about 50%). Fortunately, the major proportion of the saturated acids can be separated from the mixed fatty acids of tallow by crystallization from a suitable solvent under proper temperature conditions. Our experience indicates that this separation can best be accomplished with acetone at 0° to —20° C. The iodine number of the solid acids obtained in this way ranges from 4 to 12. These iodine values result mainly from incomplete removal of occluded mother liquor from the precipitate, but apparently at lower crystallization temperatures some unsaturated material, probably iso-oleic acid, is precipitated. The saturated acids obtained by crystallization at 0° C. usually have an iodine number of about 4 whereas the acids obtained by crystallization at —20° C. usually have an iodine number of about 12. Approximately 90% of the saturated acids in the tallow may be obtained in this fraction; this yield is considerably higher than can be obtained by conventional cold and hot pressing. These acids, obtained as glistening crystalline solids, correspond to "double- or triple-pressed stearic acid."

When crystallization of the saturated acids is conducted at —20° C., the filtrate acids have approximately the same fatty acid composition as an olive oil rich in oleic acid. These acids, which are pale yellow and have iodine numbers which range from 84 to 88, contain approximately 83 to 86% oleic acid, 4 to 7% polyunsaturated acids, and 7 to 11% saturated acids. By reaction with glycerol these acids yield a synthetic triglyceride which resembles olive oil in fatty acid composition. The preparation of a synthetic olive oil in this way offers certain obvious advantages over crystallization processes that involve fractional crystallization of natural triglycerides in which two or three different fatty acids are attached to the same molecule of glycerol. In addition, custom-made oils with a wide range of properties may be prepared by the proper selection and/or blending of various fatty acid fractions for reaction with glycerol.

By one crystallization at —50° to —60° C. of the filtrate acids referred to above an oleic acid fraction is obtained in good yield which contains about 10% saturated acids (mostly palmitic) and about 1% polyunsaturated acids. The content of the latter can be reduced to less than 0.3% by one additional crystallization. By fractional distillation under vacuum most of the palmitic acid is eliminated, and a purified oleic acid, boiling point 203-207° C./3.5 mm. (oleic acid content, above 95%) is obtained as a colorless, odorless oil. This product probably contains some isomers of normal oleic acid (3), but they are present in quantities too small to affect its suitability for most uses.

The iodine number of the linoleic-acid-rich fractions usually ranged from 105 to 110. The value of 120 (Fraction F-2, Figure 2) is unusually high. In the majority of cases over 90% of the polyunsaturated acids in the starting materials are concentrated in the linoleic fractions. These fractions may be useful for blending with other fatty acid fractions to produce low-titer products.

Figures 1 and 2 illustrate two procedures for the fractionation of tallow fatty acids.

Experimental

Starting Materials. The best grade of edible beef tallow which could be purchased was employed in the experiments reported in this paper. Various inedible grades, such as packers' tallow, are suitable, provided that the fatty acid composition and ratio of oleic to linoleic acid are satisfactory. The minimum ratio of oleic to linoleic acid for a suitable starting material is about 8:1. Some so-called tallows contain considerable proportions of other fats and hence may have a sufficiently high linoleic acid content to render them unsatisfactory for this process.

A simplified and rapid, large-scale laboratory saponification procedure was employed to obtain the

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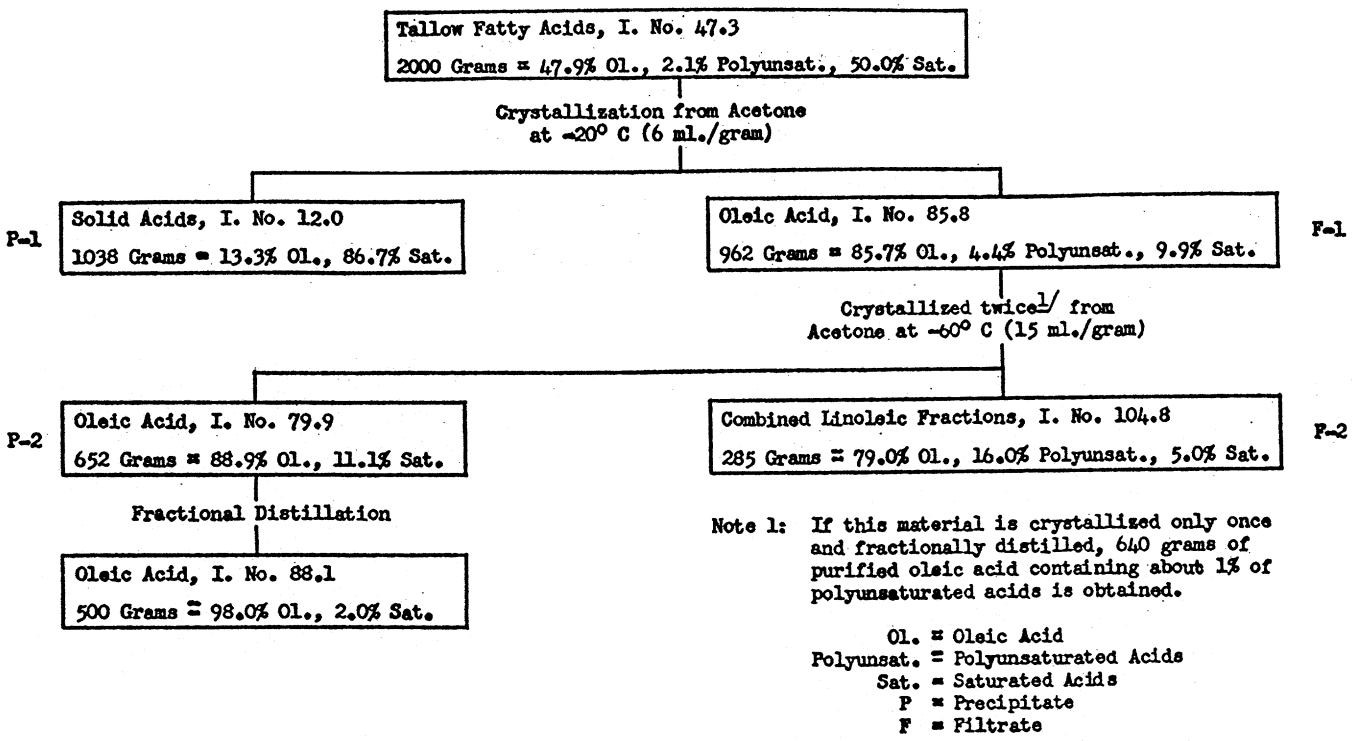

FIG. 1. Preparation of oleic acid free from polyunsaturates.

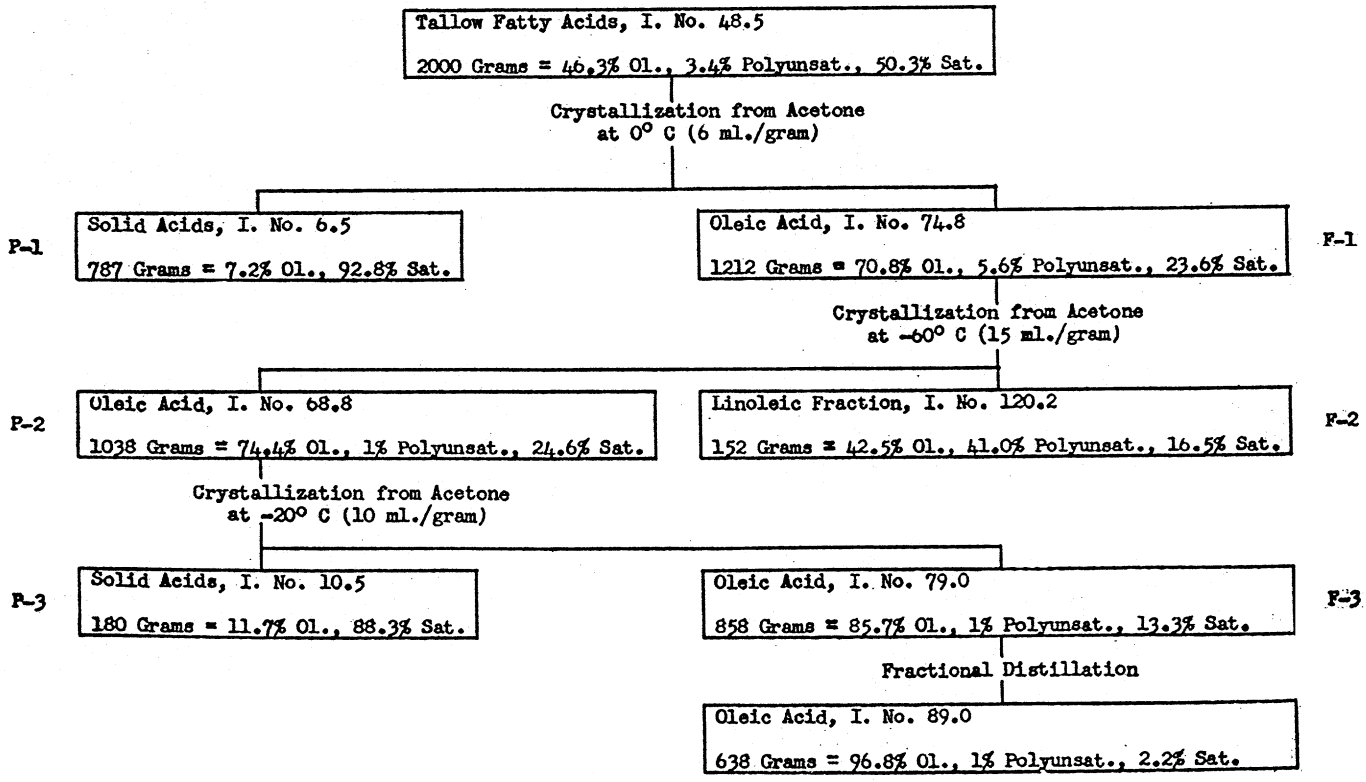

FIG. 2. Alternative method for preparation of purified oleic acid which also yields a saturated acid fraction of good quality.

acids from the fat. Ten kilograms of tallow and 10 liters of 95% ethyl alcohol were heated and stirred on the steam bath in a 50-quart stainless steel kettle until the temperature reached 60° C. The heating was then discontinued, and a 50% excess of cold 6 N aqueous sodium hydroxide was added in 1-liter portions with vigorous stirring. Each successive portion was added only after the temperature had ceased rising as a result of the reaction of the previous portion. When all the alkali had been added, saponification was usually complete, as indicated by the absence of an oily phase when a small portion of the soap solution was diluted with hot water. An excess of 6 N sulfuric acid was added slowly with stirring, and the mixture was kept at about 60° to 80° C. and stirred until the fatty acid layer was clear. The aqueous layer was siphoned off and discarded, and the oily layer was washed with hot water until free of sulfuric acid. The fatty acids were dried by heating to 100° C. under moderate vacuum in a stream of inert gas. Yields of fatty acids were quantitative. This saponification procedure has been successfully applied to a variety of fats and oils. The percentage of polyunsaturated acids in the mixed fatty acids was determined spectrophotometrically (4). The fatty acid composition was calculated from the iodine number and the known content of polyunsaturated acids.

Fractionation Procedure. The apparatus and procedure described in a previous publication (2) were employed, except that an 11-plate Vigreux column was substituted.

Preparation of a Synthetic Olive Oil. An oleic-acid-rich fraction (iodine number, 87.7; 83% oleic acid, 6% polyunsaturated acids, 11% saturated acids) prepared by crystallization of tallow fatty acids at —20° C. (see comparable Fraction F-1, Figure 1), after straight-run distillation to remove color, was reacted with slightly less than the calculated quantity of anhydrous glycerol at 190° C. in an inert atmosphere and under vacuum until the acid number of the mixture became constant. The unreacted oleic acid was separated by vacuum distillation. The synthetic triglyceride, obtained in almost quantitative yield, was a pale-yellow oil with the following characteristics: iodine number, 84.2; acid number, 3; melting point, <0° C.

Summary

Tallow fatty acids have been fractionally crystallized from acetone at temperatures ranging from 0° to —60° C.

By crystallizing at 0° to —20° C., a saturated acid fraction which amounts to 40 to 50% by weight of the starting material has been obtained. This fraction corresponds to "double- or triple-pressed stearic acid."

The filtrate acids from the crystallization at —20° C. contain over 90% of the oleic acid present in the starting material, and in fatty acid composition this mixture is similar to olive oil. From this fraction, which amounts to about 50% by weight of the starting material, a synthetic triglyceride with properties approximating those of olive oil has been prepared.

By low-temperature crystallization of this oleic-acid-rich fraction at —50° to —60° C., followed by fractional distillation, a good yield of purified oleic acid (oleic acid content, over 95%) has been obtained.

REFERENCES

1. Brown, J. B., Chem. Reviews *29*, 333 (1941).
2. Swern, D., Findley, T. W., and Knight, H. B., Oil and Soap *21*, 133 (1944).
3. Millican, R. C., and Brown, J. B., J. Biol. Chem. *154*, 437 (1944).
4. Brice, B. A., Swain, M. L., Schaeffer, B. B., and Ault, W. C., Oil and Soap *22*, 219 (1945).